A 1.2 cm E. P. R. SPECTROMETER AND PARAMAGNETIC RESONANCE IN SOME COPPER SALTS

U. S. GHOSH, R. N. BAGCHI AND A. K. PAL

DEPARTMENT OF MAGNETISM, INDIAN ASSOCIATION FOR THE CULTIVATION OF SCIENCE, CALCUTTA-32

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ABSTRACT. A transmission type e.p.r. spectrometer operating at 1.28 cm wavelength, set up in our laboratory from purchased and constructed components is described in details. Resonance absorption signals at room temperature for some concentrated paramagnets have been obtained with a small noise-to-signal ratio. Orthorhombic g-values and orientations of the tensor ellipsoid of single crystal of $CuK_2(SO_4)_2 \cdot 6H_2O$ have been determined at room temperature and some features of e.p.r. spectra of two copper salts have been discussed.

INTRODUCTION

If a steady magnetic field H is applied on a paramagnetic substance, the energy levels of the paramagnet (electron, atom, ion, molecule or radical) which were initially degenerate split into the so-called Zeeman levels, the energy separation $E_1 \sim E_2$ between successive Zeeman levels being given by $g\beta H$ where β is the Bohr magneton, and g is the spectroscopic splitting factor. With magnetic fields of a few thousand gauss the energy values of the Zeeman splittings fall in the microwave range of electromagnetic radiation. Thus, microwaves falling upon paramagnets under such static magnetic fields will under certain conditions provide the requisite energy for transitions between the successive Zeeman levels so that on an average the population of the upper levels increases and a net characteristic absorption of microwaves occurs. For the transitions to occur it is evident that the energy of the incident microwave radiation $h\nu$ should be equal to the separation $g\beta H$ of successive Zeeman levels i.e. $h\nu = g\beta H$ and the maximum transition probability is obtained when the microwave field is perpendicular to the static magnetic field.

It very often happens that the internal fields in a paramagnetic crystal splits up the energy states to more or less extent and the introduction of the external static magnetic field only serves to enhance these splittings to an extent just needed to be spanned by a given microwave energy. In this case the relationship between the so-called zero field splitting superposed Zeeman splitting and the microwave energy is more complicated.

DESCRIPTION OF THE COMPLETE 1.2 CM MICROWAVE SPECTROMETER

(1) The complete experimental set-up is shown in a block diagram in Fig. 1. A few of the wave guide components, klystron power pack, klystron and other

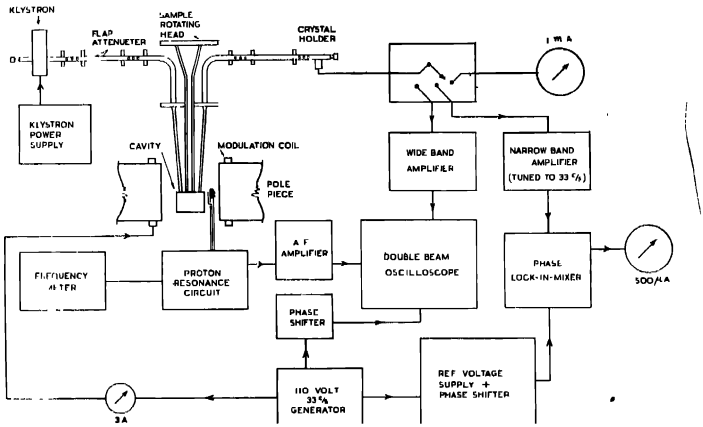


Fig. 1

accessories were purchased as in pieces and others such as flap attenuator, probe tuner, waveguide bends, low temperature distrene filled german silver guides, cavity reasonator, crystal holder, modulation coils, phase sensitive detector, proton resonance fluxmeter, low temperature tuning assembly, narrow band amplifier, waveguide couplers, waveguide bench etc. were made in the laboratory.

The 1.2 cm spectrometer employs a 2K33 reflex klystron tube as the source of microwave power Appropriate stabilized voltages have been supplied to the resonator, reflector and grid of the klystron from an electronically stabilized power pack (P.R.D. type 801 A, universal klystron power supply), the filament being heated by 6 volt a.c. obtained from the same power pack. TE_{10} mode is excited and propagated after proper tuning by the klystron tuner and tuning screws along the '*K*' band wave guide (1.064 cm $\times$ 0.432 cm) with suitable attenuation by a flap attenuator. The incident microwave power then passes through an H-bend section (bent in the plane of magnetic lines of force) of the waveguide and is fed into the cavity reasonator through a distrene filled thin walled German silver wave guide of appropriate smaller dimension, namely, 6.0 mm $\times$ 2.5 mm. A cylindrical brass cavity resonator operated in TE_{111} mode has been used in order to concentrate the microwave field energy in the sample placed inside the cavity. The distrene filled *g.s* guides have been used to minimise the dimension of the

guide and hence the leakage of heat inside the cryostat in which the cavity is placed for low temperature work. The narrow g.s guide is matched with the *H*-bend of normal size through a tapered g s. section of length 5.5 cm. and taper-angle of 7° along the borad face. The part of the distrene within this section is oppositely tapered ending as a point where the g.s guide taper just starts. The internal diameter of the cavity is 1.3 cm and the cavity length can be varied from 4 cm to 12 cm by means of a tuning choke plunger at its bottom running in a fine screw thread and being operated from above through a gear system by a thin stainless steel shaft. Elliptical iris hole (2.5 mm × 1.5 mm approximately) at the top surface of the cavity is used to couple the g s. guide to and feed microwave signal into it. The output signal from the cavity is taken through another similar distrene filled German silver guide coupled to the cavity and an H-bend section as before. A long thin stainless steel tube of 5 mm internal bore is coaxially fixed into a hole at the top surface of the cavity. A microwave choke attached to another stainless steel tube of smaller diameter can be easily lowered until the end face of the choke becomes flush with the inside top of the cavity, a graduated circular disc with a vernier scale is fixed at the top of this tube, so that it can be rotated through any desired angle about the cone fitting between the two tubes just below the disc. The face of a single crystal sample in which the measurement is to be taken, is placed flat upon the end face of the choke and fixed to it with a thin layer of vacuum grease. The static magnetic field remains always parallel to the end face of the choke which lies in the region of maximum concentration of microwave field at TE_{111} mode. If the specimen is magnetically isotropic it can also be placed at the centre of the tuning plunger. Tuning screw matching is provided in the wave guide run before and after the input and the output *H*-bend sections respectively. The complete assembly of H-bends, German silver guides and the cavity resonator is shown in Figure 2.

The transmitted microwave power from the cavity resonator is detected by a silicon-tungsten crystal, type IN 26, mounted inside the crystal holder section of the guide coupled to the output H-bend. The rectified output from the crystal detector is taken off through a co-axial line. For optimum performance of the crystal the rectified crystal current is usually kept near .5 mA by adjusting the attenuator.

(ii) *Magnet* :

The cavity is placed in the central region of the variable gap between the pole faces of a strong electromagnet supplied by Newport Instrument Ltd. (England). The electromagnet is capable of producing a highly homogeneous and constant field of maximum value 9000 oersted with 10 cm diameter pole face and 2 3 cm gap, at a continuous rating of 4 amperes delivered from a 220 volt battery of lead accumulators through a series of rough and fine control rheostats. With a pair of auxiliary coils wound over brass spools with 750 turns of D.C.C wire (S.W.G.

No 20) in each and mounted round the poles the steady magnetic field can be sinusoidally modulated at 33c/s. 33c/s is obtained from an 110 volt 2 kw alter-

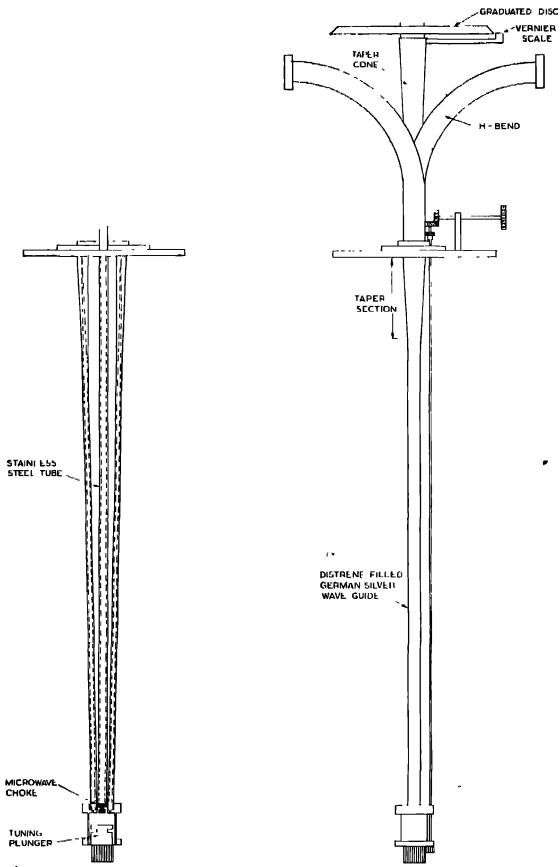
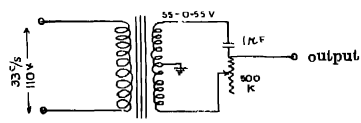


Fig. 2.

nator driven by a D.C. motor, the D C voltage being supplied from a stable 220V, 15 kw D.C generator with a constant voltage transformer at its input The modulation amplitude of the field can be varied by changing the current given to modulation coils with a variac. The maximum modulation field is found to be nearly 250 gauss.

(iii) *Detection and measuring system*

(*a*) *Vide o-detection method* In video-detection system the whole width of an absorption signal is covered by the 33 c/s modulation sweep applied to the steady magnetic field which is brought to the resonance value The rectified current from the crystal detector will then consist of a function representing the shape of the absorption signal recurring at twice the modulating frequency since absorption of microwaves will occur when the resonance value of magnetic field is attained both during the forward and backward sweep of the modulation. The absorption signal from the crystal detector is fed to a wide band amplifier (by M/s Solartron Ltd , England) having the proper input impedance (600 ohms) required to match the impedance of the detector crystal, of sufficient bandwidth (15 c/s–300 kc/s) to pass almost all the Fourier components of the absorption signal and thus to pass the signal without any distortion of its shape. The output from the amplifier is applied to the *Y*-plates of Cossor no. 1049 blue trace double beam oscilloscope, the time base being fed at the modulating frequency via a phase shifter, the circuit diagram of which is shown in fig. 3.



Phase shifter

Fig. 3 Out put to External time base of Oscilloscope (cossor)

Two traces of the signal appear on the C R O. screen corresponding to the forward and backward sweep, which are brought to coincidence by adjusting the phase shifting circuit. The steady magnetic field is then adjusted to bring the two coincident peaks just at the centre of the horizontal trace of the oscilloscope This corresponds to the exact resonance value of the steady magnetic field Although this video-detection method is suitable in the case of narrow lines, it presents many difficulties for a line width of 50 gauss or more, which is very common with the concentrated salts of the iron group we want to study Apart from the troubles arising out of the unavoidable 50 c/s pick up and crystal and circuit noises, wide lines will introduce additional troubles in requiring large enough depth of modulation and very large bandwidth of the amplifier stage for undistorted display of the signal shape

(b) *Phase-sensitive detection method* . For wide lines phase sensitive detection (p.s.d.) method has been adopted and the difficulties mentioned above are thus got rid of to a large extent In this method the steady magnetic field is modulated by a small magnetic field varying sinusoidally at 33c/s and having an amplitude equal to a very small fraction of the total line width. The steady field is then gradually and slowly increased so that each part of the whole absorption

line is successively swept. When the steady field reaches a value in the neighbourhood of resonance, a 33 c/s component of the detector current will appear. The amplitude of this component will be proportional to the slope of the absorption curve at any particular value of the steady field. By mixing this 33 c/s signal at proper phase with a reference signal of same frequency and adjustable phase, which can be viewed as a gating signal and is obtained from the same modulating source, a *d-c* output will be obtained proportional to the slope of the absorption curve at each point. When the static field slowly sweeps the whole of the absorption line, this *d-c* output will be a derivative response of the absorption signal. The *d-c* output thus obtained in the phase lock-in mixer circuit (Fig.

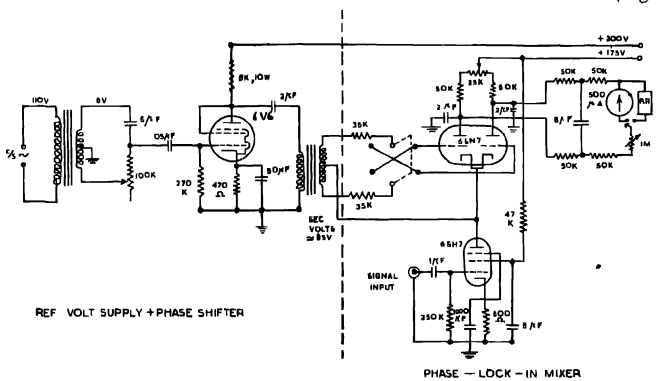
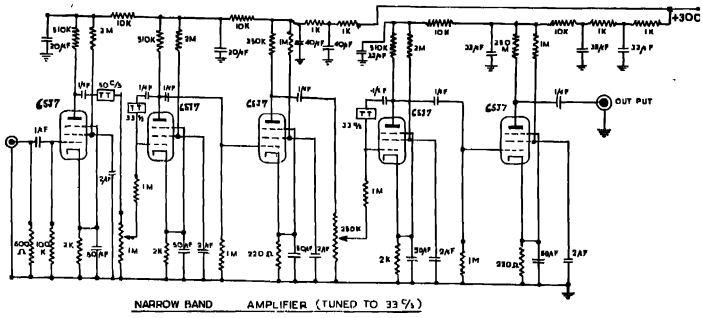


Fig. 4. Phase Sensitive Detector

designed after Schuster (1951) is finally fed to a centre-zero microammeter (500μA) or to a pen recorder via a long time constant *R-C* net work which eliminates any noise or fluctuation coming with the signal, the time constant depending on the rate of variation of static magnetic field. The phase lock-in mixer is preceded by a narrow band amplifier tuned to 33 c/s so that the 33 c/s sinusoidal output from the crystal detector first passes through it (circuit diagram shown in Fig. 5). This tuned pre-amplifier eliminates most of the a.f. and r.f. crystal noises and 50 c/s pick-up. The position of an absorption peak is indicated in the derivative response when the centre zero microammeter needle crosses the null position after reaching one extremity as we slowly increase the magnetic field. The static magnetic field is kept in this position if we want to measure the exact resonance value of the magnetic field.

MEASUREMENT OF THE MAGNETIC FIELD

The magnetic field is measured with the help of a proton resonance (p.r.) fluxmeter (Fig. 6) designed mostly after Knoeble and Hahn (1948). 0.12 molar



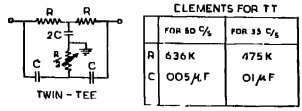


Fig. 5.

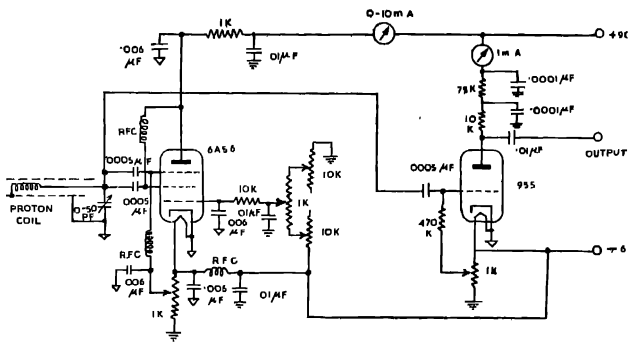


Fig. 6. Proton Resonance Circuit.

$Fe(NO_3)_3$ solution in a narrow cylindrical capsule of pyrex glass is used as the proton sample. The proton probe is a simple rigid co-axial cable carrying the capsule at one of its end; a few number of turns of S..W.G No. 30 enamelled copper wire are wound over the capsule with one end connected to the central conductor and the other to the outer shield of the co-axial cable. The proton sample is placed very near the cavity within the central region of the pole faces such that the coil wound over the narrow capsule and the experimental specimen inside the cavity occupy symmetrical position between the pole faces. It has been found that within a range of 1 cm the value of the magnetic field in the central region

remains everywhere the same within 1 part in 10,000 as seen from the unchanged position and shape of the proton resonance (p.r.) signal in the C R O.

METHOD OF MEASUREMENT OF THE P.M R. PEAKS IN SINGLE CRYSTALS

In actual measurement the experimental sample a, single crystal, is placed with a given plane horizontal on the end face of the microwave sample holder choke as explained earlier, a standard sample of the free radical D.P P.H. (diphenyl picryl hydrazil) is placed at the centre of the tuning plunger of the cavity and the proton probe just outside the cavity in a manner explained above. All these are then within a range of 1 cm and the magnetic field is the same at each of them. The D P.P.H. sample holder is a very thin and small perspex plate over which few grains of D.P.P H. are spread and fixed by a thin layer of duro-fix.

In video-detection system the p.m.r. signal is fed to one beam of the double beam C.R O via a wideband amplifier and the p r. signal to the second beam via an audioamplifier The radio-frequency at which proton resonance occurs can be varied by adjusting a variable condenser in the r f oscillator so that the peaks for the two resonance signals coincide at the centre of the C.R.O. for the given static magnetic field at which paramagnetic resonance peak occurs. This p.r. frequency is then measured very accurately correct up to 1 part in 10^4 by a heterodyne frequencymeter (Signal Corps, BC-221—AH) having crystal check points. Measuring the p r. frequencies at different static magnetic fields corresponding to *two P M R. signals* one for the experimental specimen and the other for the standard D P P H sample, we can easily calculate the g-values of the specimen along the direction of the applied magnetic field as follows : When the proton signal is made to coincide with the P M R. signal for the specimen we will have

$$g\beta H = h\nu \qquad \ldots \quad (1)$$

$$g_N\beta_N H = h\nu_N \qquad \ldots \quad (2)$$

where g and g_N are the g-values for the specimen and the proton (nuclear g-factor) respectively, β and β_N are atomic and nuclear Bohr magnetons, and ν and ν_N are the microwave and radio frequency respectively. Similarly, when the proton signal is made to coincide with the P M R signal corresponding to D.P.P.H. occurring at a different magnetic field, the microwave frequency remaining unchanged we will have

$$g_D\beta H' = h\nu \qquad \ldots \quad (3)$$

$$g_N\beta_N H' = h\nu_N' \qquad \ldots \quad (4)$$

From equations (1), (2), (3) and (4) we get the g-value of the specimen to be

$$g = g_D \cdot \frac{\nu_N}{\nu_N} = 2.0023 \frac{\nu_N'}{\nu_N} \qquad \ldots \quad (5)$$

[g-value for D.P.P.H is accurately known to be 2.0023 (ref. Ingram, 1955)]. It is obvious from above that any variation of the steady magnetic field during the measurement will not affect the result, provided the microwave and r.f. frequencies remain constant.

In the p.s.d. method used in the case of wide lines, the small modulation amplitude is sufficient to sweep through the whole of the proton or D.P.P.H. signal which are both quite narrow. Hence the proton signal can be displayed on the C.R.O. screen, while the steady magnetic field is kept at resonance value for the experimental specimen in a manner explained earlier by observing the zero position of the microammeter in p.s.d. out-put. The p.r. frequency is measured as in the previous case. Equations (1) and (2) will also now hold good. Again making the proton signal to coincide with the P.M.R. signal for D.P.P.H. in the C.R.O. and measuring the p.r. frequency under this condition we will have the conditions of equations (3) and (4) fulfilled. Thus from these two measurements of p.r. frequencies we can calculate the g-value of the specimen with the help of equation (5). Any change in the magnetic field during the measurement of p.r. frequency corresponding to the p.m.r. of the specimen will be indicated by the unbalance of the centre-zero microammeter (500μA) from its null position.

The line width can also be obtained directly from the separation of the maximum and minimum of the derivative curve in the case of well resolved lines, otherwise the full absorption signal is to be obtained after numerical integration of the derivative curve. This is best done with the help of a pen-recorder. Due to the lack of such an instrument the linewidth has not been quantitatively measured although a qualitative idea can be obtained from the C.R.O. display of the signal or from the derivative response of the centre-zero microammeter.

RESULTS AND DISCUSSION

C.R.O. display of p.r. signal and P.M.R. signals for D.P.P.H, single crystals of $CuSO_4$, $5H_2O$(triclinic) and $CuK_2(SO_4)_2$, $6H_2O$ (monoclinic) are shown in Figs. (7), (8), (9) and (10) respectively. In the photographs the return trace of the oscilloscope is blacked out.

In the case of $CuSO_4$, $5H_2O$ figure (9) shows the absorption signal, when the magnetic field is applied along a particular direction, parallel to the (110) face of the crystal, in which it is most prominent. The line width shows an angular variation becoming so large in some orientations that the signal gets completely ill-defined for C.R.O. display (c.f. Bagguley and Griffiths, 1950). In this case we were unable to resolve the two lines for the two ions in the different planes even with p.s.d. method at 1.2 cms and 300°K and hence the principal ionic g values and their orientations could not be measured. We are trying to do this by setting up a 0.8 cm spectrometer.

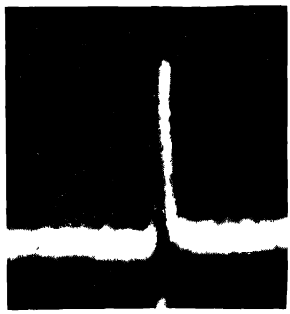


Fig. 7. Proton Signal

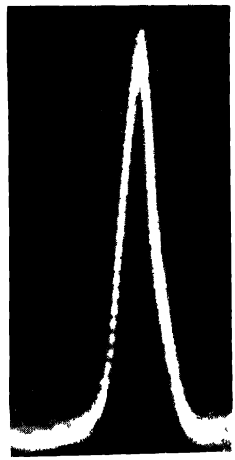


Fig. 8 Signal for D.P.P.H.

Fig. 9.
Signal for $CuSO_4\ 5H_2O$

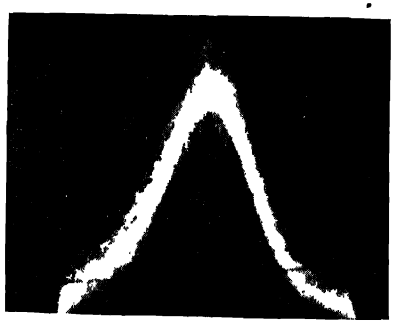


Fig. 10
Broad Signal for $CuK_2(SO_4)_2\ 6H_2O$.

In the case of the single crystal of $CuK_2(SO_4)_2 6H_2O$ the absorption signal is too broad to be very faithfully displayed on the C.R.O. screen although the peak could be recognized for all orientations of the crystal. With the p.s.d. method it was possible to determine the positions of the peaks very clearly for the resolved lines. In general for any orientation of the crystal two signals appear due to the two inequivalent ions* in the unit cell obtained from one another by a reflection

* Crystallographically equivalent.

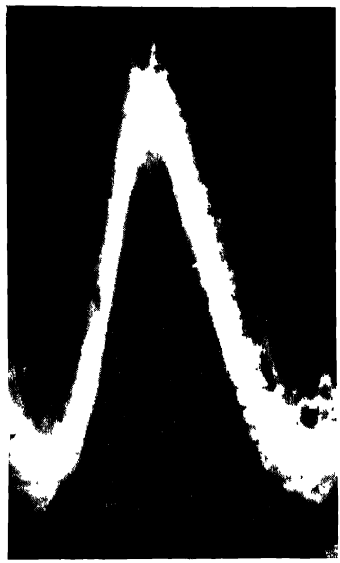


Fig 11

Narrow Signal for $CuK_2(SO_4)_2.6H_2O$ (Photographs in Fig 9, 10, 11 taken under identical modulation amplitude).

in the (010) plane. The linewidth also shows angular variation, (cf. Bleaney *et al.*, 1949) the amount of variation being less than in the case of $CuSO_4\,5H_2O$. From the measurement of g values in different directions along four simple planes of the crystal (mostly natural faces) g values have been calculated directly by a convenient method analogous to the determination of principal susceptibilities in triclinic crystals (Ghosh and Bagchi 1962) developed by us and to be discussed in details in a further communication. The principal ionic g-values in $CuK_2(SO_4)_2.6H_2O$ show that the symmetry of the crystalline electric field is definitely orthorhombic rather than tetragonal (c.f. Bleaney *et al.*, 1949) The principal g values at room temperature (300°K) and their orientations in usual tensor notations, with reference to the crystallographic axes, are shown in Tables I and II respectively.

These values are consistent with the results of Bleaney *et al* (1949) at 90°K calculated indirectly by trial.

It appears that g values do not differ much for these two temperatures indicating that the crystal field remains almost unaltered in this range of temperatures.

TABLE I

	This paper	Bleaney *et al.*
G_1	2 16	2.14
G_2	2 05	2 04
G_3	2.38	2 36

TABLE II

c^* is a line normal to 'a' and 'b' axes of the monoclinic crystal

	a		
G_1	54°5′	134°6′	114°24′
G_2	72°50′	106°56′	24°30′
G_3	41°6′	48°59′	92°

The fact that the signals for the two inequivalent ions in the unit cell are resolved in the case of $CuK_2(SO_4)_26H_2O$ and in no orientation the line width is small enough to be very faithfully displayed on the C.R.O. screen,unlike the case of single sulphate of copper for which the line width is comparatively much less in some orientations although signals for two inequivalent ions are not resolved, suggests that exchange interaction effects are more prominent in $CuSO_4$, $5H_2O$ than in $CuK_2(SO_4)_2$, $6H_2O$ (cf. Bleaney *et al*, 1949).

It is known that magnetic dipole-dipole interaction between paramagnetic neighbours broadens the lines Exchange interaction between similar ions i.e. ions with the same energy and parallel precessional axes of spin vectors in the applied magnetic field produces a narrowing of the line, while exchange interaction between dissimilar ions adds to the dipolar broadening (Gorter and Van Vleck, 1947). In the second type of exchange, if the interaction energy between two neighbouring ions is less than the separation in energy of the two ions in the applied magnetic field, two lines will appear corresponding to the two ions (Pryce, 1948). Hence the narrow unresolved signal of $CuSO_4$, $5H_2O$ at least qualitatively indicates that both types of exchange forces are much stronger in single sulphate of copper than in copper potassium sulphate This is expected considering the closer proximity of neighbouring copper ions in $CuSO_4$, $5H_2O$ and agrees with the earlier findings.

Further, it is readily found from the C.R.O. display or from the derivative response that the signal for $CuK_2(SO_4)_26H_2O$ in (001) face shows a definite narrowing of the peak to some extent in some orientations (Figs. 10 and 11) This occurs whenever the two signals corresponding to two ions are coincident i.e. whenever the direction of applied magnetic field is equally inclined to the corresponding principal axes of the two ions (the magnetic field is then either along 'a' or 'b' axis of the crystal). In such a situation the magnetic energy of the two ions in the applied magnetic field is the same although the spin vectors of the two ions may not precess about parallel axes. Under such condition exchange broadening will be much less and apparent narrowing of the line will result, the degree of such narrowing being much less in this salt than in $CuSO_4$, $5H_2O$ as seen readily from

oscilloscope dislpay or derivative response of the signal. This suggests that in $CuK_2(SO_4)_26H_2O$ exchange forces, although weaker in strength, are not negligible.

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